PATENT
Attorney Docket No. 401577/Y.P. LEE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Appln. of:

KIM et al.

Application No. 10/092,468

Filed: March 8, 2002

Art Unit: 1626

Examiner: Laura Lynne Stockton

For: METHOD FOR PREPARING AND USES OF CUCURBITURIL DEVICES

DECLARATION UNDER 37 CFR § 1.132 FROM KIMOON KIM

Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

I, Kimoon Kim, hereby declare that:

1. I am a named co-inventor of the above-identified application, and am familiar with the application and pending claims.

2. I received a Bachelor of Science degree in Chemistry from Seoul National University, in Seoul, Korea, in February of 1976, and a Master of Science degree in Chemistry from Korea Advanced Institute of Science and Technology in February of 1978. I received a Doctor of Philosophy degree in Chemistry from Stanford University in 1986. After postdoctoral work at Northwestern University, I joined Pohang University of Science and Technology where I am presently a Professor of Chemistry. I am also the director of the Center for Smart Supermolecules (CSS) supported by the Creative Research Initiative Program of the Korean Ministry of Science and Technology.

3. The United States Patent and Trademark Office has rejected claims 6-24 under 35 U.S.C. § 103 (a), as allegedly unpatentable over Kim et al. (J. Amer. Chem. Soc., 122, 540-541 (2000)), Buschmann et al. (DE 19603377), and Flinn et al. (Angew. Chem. Int. Ed. Engl., 31, 1475-77 (1992)), either alone or in combination with each other. The accompanying declaration addresses why Kim et al. should not be applied. In the present declaration, based on the experimentation conducted under my supervision, the results of which are discussed below, it is my opinion that the presently claimed invention has unexpected or superior properties relative to the subject matter of Buschmann et al. and Flinn et al.

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4. The presently claimed invention provides a greater range of useful products. As set forth in Table 1 below, the cucurbituril (CB) derivative obtained in the method of Buschmann et al. is 100% CB6 (hexamer). In contrast, the CB derivatives obtained according to the methods of the presently claimed invention range from CB5 to CB11, which are desirable in the industry.

Table 1

		Preparation method of Buschmann et al.[a]	Preparation methods of presently claimed invention		
			Method 1[b]	Method 2[c]	Method 3[d]
Reaction conditions		conc. H_2SO_4, 135-165°C, 12 Hr	(1) 9M H_2SO_4, 70-75°C, 24 Hr (2) 100°C, 12 Hr	(1) Separation of linear oligomer: 12M HCl, 75°C, 20 min (2) 11M H_2SO_4, 80°C, 12 Hr	(1) Separation of linear oligomer: 90°C (2) 10M H_2SO_4, 80°C, 12 Hr
Ratio of CB[n] (%)	CB[5]		10	14	15
	CB[6]	100	57	55	42
	CB[7]		20	20	26
	CB[8]		10	8	12
	CB[9]-[11]		3	3	5

a: The preparation method of Buschmann et al. was carried out under the same conditions as in Example.

b-d: Preparation methods 1-3 of the present invention were carried out in the same manner as in Synthesis Example 5 of the patent application. In Table 1, (1) represents a linear oligomer formation reaction, and (2) represents a cyclization.

5. Further, the presently claimed invention has a superior property. As set forth in Table 2, the dye removal efficiency of the CB derivatives of the present invention is higher than that of Buschmann et al. and Flinn et al. "Ratio" denotes a quantitative value of the dye removal efficiency of CB [n], and the smaller the value, the better the organic dye removal efficiency.

Ratio (%) = {(Absorption intensity of organic dye solution after treatment with CB[n]x100)} / (Absorption intensity of organic dye solution before treatment with CB[n])

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Table 2

Dye	Ratio (%)				
	Buschmann et al. CB[6]	Inventive CB[7]	Inventive CB[8]	Decamethylcucurbit[5]uril of Flinn et al.	Mixture of 5-30% inventive CB[5] derivative, 30-70% inventive CB[6], 5-30% inventive CB[7], 2-15% inventive CB[8] and 1-10% CB[9]-[11]
Direct Red 5B	13	1.7	1.1	32.2	1.9
Reactive Blue HE-G	7.2	0.3	0.3	21.0	0.3
Direct Solophenyl Violet 4BL	13	1.3	1.1	31.1	1.2
Reactive Navy Blue HE-R 150	9.0	0.6	0.6	24.8	0.5
Disperse Yellow E-3	18	3.0	3.0	37.1	2.8
Disperse T/Q Blue S-GL 200	8.9	0.8	0.8	25.1	0.9
Orange TGL	25	5.4	5.6	42.5	4.5

Referring to Table 2, the organic dye removal efficiencies of CB[7] and CB[8] according to the present invention, and the composition claimed in claim 8 are higher than those of CB[6] of Buschmann et al. and decamethyl CB[5] of Flinn et al. The cucurbituril derivative compositions according to the present invention are advantageous in that they can be directly used in various applications without separate purification.

6. We hereby declare that all statements made herein of our own knowledge are true, that all statements made on information and belief are believed to be true, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

March 15, 2003

Date

Kimoon KIM

DE 19603377A1

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The isolation of Behrend's polymer and the separate transformation of the polymer to Cucurbituril with the stand of technology lead to higher quantity of chemicals and to less yield. The mission is to invent with the stand of technology, a process for the synthetic production of Cucurbituril with huge yield and with big process security. To solve the mission serves the marks of pretension 1.

The invention:

Acetylenediurea (Glycoluril) in aqueous solution of a strong inorganic acid in presence of excess formaldehyde to solvent with heating and synthesis Berend's polymer through evaporation of the water.

The water will be removed through evaporation, without intermediate stage, complete and the delude polymer-solvent through heating shifts to Cucurbituril. If you start with acetylenediurea, the monomeric building block of Cucurbituril, will be synthesis of Cucurbituril in one step. Through evaporation of the solvent (water), the reaction mixture run through the reaction conditions of all steps one after another. Therefore escapes the isolation of the intermediate products and the yield will be bigger. The yield is 80-85 % with the new synthesis. In comparison to the method and the beginning collect with a yield between 40 % and 70 %. Now the yield is very bigger and the fluctuation broad is smaller.. Because Cucurbituril can be used technically in the cleaning of colored waste water, it has a big economic role. The arised crystal pulp are cooled and then pooled in cool water. At first the Cucurbituril solves, then it precipitates than heavy fine crystal sediment. You can step up the yield, if you cooks it short or you wait a time space, ½ hour to 2 days.

New more advantage sign of the invention.

The synthesis of Cucurbituril in separately described:

Acetylenediurea is obtainable commercially or it can be synthesized easily from glyoxal and urea, acid-catalyzed. Acetylenediurea solves in aqueous sulfuric acid with an excess of formaldehyde through heating and through evaporation of the water, it reacts to Berend's polymer. The water will be removed without intermediate stage complete through evaporated, and the remained polymer solvent through heating transformed to Cucurbituril under elimination of formaldehyde. The quantity of the used concentrated sulfuric acid is dependent of the handling. Is the quantity to small,

probable the transformation to Cucurbituril is incomplete, so that the synthesis of Cucurbituril impure with polymers and oligomer. Is the quantity of sulfuric acid to huge, the yield decrease to, because the solubility of Cucurbituril depends by the acid concentration, then it stay in filtrate. The viscosity of the crystal pulp is dependent on the acid concentration, too.

The quantity of the used "reaction water" influences only the transformation of the Berend's polymer. The more water you use, the more yield you get. The used water quantity depends by the economy efficiency, because you must eliminates all water through evaporation and heating. The arised crystal pulp are cooled and then pooled in cool water. At first the Cucurbituril solves, then it precipitates than heavy fine crystal sediment. The sediment quantity are dependent by the quantity of the "precipitate water", in which the crystal pulp solves. The increase is very small, if the water quantity are more than 10 : 1 in comparison with the sulfuric acid quantity. You can step up the yield, if you cools it short or you wait a time space (1/2 hours to 2 days). The sediment will be filtered, washed with water acid-free and dried. On the dried temperature over 100 °C, you eliminate the most bound water. With this method, you can reach the yield over 80 %.

The synthesis of the Berend's polymer is possible with other acid, but the transformation to Cucurbituril are possible only with sulfuric acid, because it owed important structure-formed property.

In a variant process:

The crystal pulp will be dilute in concentrated sulfuric acid with water until it solves completely. The solution will be under strong stirring added a inert support medium, like mineral oxide, like silica gel and aluminum oxide and organic polymers. If after that water added, the Cucurbituril sedimentate on the support medium.